A DEGRADATION STUDY FOR DISLODGEABLE METHAMIDOPHOS (MONITOR) RESIDUE ON BROCCOLI AND CAULIFLOWER FOLIAGE IN SAN LUIS OBISPO AND SANTA BARBARA COUNTIES, CALIFORNIA

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SUMMARY

Four fields (1 broccoli and 3 cauliflower) in the Santa Maria Valley of San Luis Obispo and Santa Barbara counties, were sampled for dislodgeable foliar pesticide residue after a application of methamidophos (Monitor). Samples were collected before the applications and throughout the reentry intervals for specific crop/pesticide combinations. As an interim measure (until data gaps are filled) a "safe level" of 660 ng/cm^2 (0.66 ug/cm^2) of residue has been set. At this level unprotected field workers could enter a field with little hazard. This level was never exceeded in any of the fields studied.

INTRODUCTION

Methamidophos (O,S-dimethyl phosphoramidothioate, Monitor^R) is a Toxicity Category I organophosphate insecticide used extensively in agriculture. methamidophos has an acute oral LD_{50} (rat) of 7.5 mg/kg and an acute dermal LD_{50} (rat) of 50 mg/kg (NIOSH, 1979). The most common adverse effect of organophosphate poisoning is cholinesterase inhibition, which may lead to such symptoms as nausea, vomiting, dizziness, etc.

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations (California, 1982). A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into a treated area. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a residue level of low hazard. The adequacy of these safety intervals has not been completely evaluated since their introduction. This study was initiated to validate the existing reentry interval for methamidophos. The objective of this study was to determine the foliar decay rate and the time when worker reentry may occur. This study is one of several studies conducted for reentry interval validation.

MATERIALS AND METHODS

Cooperation was obtained from pest control operators (PCO's) and growers who would be using Monitor^R. The material used was Ortho Monitor 4 Spray, EPA Reg. No. 239-2404 AA, registered by Chevron Chemical Company. The material contains 40% active ingredient (methamidophos), with a maximum application rate of 2 pints of formulated material per acre. The application rate used in these studies was 1 pint in fields #1 and 4 and 2 pints in fields #2 and 3 (1/2 to 1 pound active ingredient) per acre. The dilution rate was 50 gallons of water per acre.

The current reentry interval for fields treated with products containing methamidophos is 24 hours. In this study, other organophosphates were applied with Monitor^R extending the reentry interval to 60 hours. Monitor^R was applied in combination with Systox in field #1 and with Metasystox-R in fields #2, 3 and 4. All applications were made by ground spray equipment to the fields.

The selected field was divided into three areas. Non-adjacent rows from each of these areas were chosen as the sample rows. These rows were designated A, B, and C. Each sample consisted of a composite of leaf punches from each of the three rows. Each sampled row was marked at the beginning of the row and at the locations of the first plant and last plant sampled in that row. Sixteen leaf punches (each 2.54 sq. cm. in diameter) were taken from each sample row; eight on the right entering the row, and eight on the left exiting the row. Punches were taken from leaves presenting the greatest exposed surface area. Each sample contained 48 leaf discs accumulated in a four ounce glass jar. The leaf punch was cleaned with alcohol between row samplings. Three replicate samples were obtained simultaneously at each sampling interval. Sample jars were sealed with aluminum foil, capped, and stored on wet ice. The ice was constantly replenished to insure temperature stability.

One set of samples were collected prior to the application. Post-application samples were taken after the materials had settled and/or dried; at 24 hours, 48 hours, 72 hours, and at 6 days after the application.

Samples were shipped on wet ice to Chemistry Laboratory Services in Sacramento for next-day analysis. The procedure for gas chromatography (GC) analysis of methamidophos is given in Appendix I. The minimum detectable level for methamidophos is 2 ng/cm^2. Weather conditions were mostly clear and sunny, with some light rainfall. The high temperatures ranged from 62° to 72°F with lows ranging from 39° to 46°F.

RESULTS

The results for methamidophos residue analysis are given in Table 1. The dislodgeable residue decay rates are illustrated in Figure 1. Knaak, et al. (1980) has calculated "safe levels" of dislodgeable residue for certain pesticides. This is a level of foliar residue in which an unprotected field worker could reenter a treated area with little or no hazard. A safe level has not been calculated for methamidophos; but, by comparing dermal LD_{50} values with chemicals that do have calculated safe levels, a safe level can be estimated (Maddy, 1985). This level for methamidophos is 660 ng/cm^2. Residues found in this study never exceeded this estimated safe level in any of the fields.

DISCUSSION

The residue levels degraded as expected in all fields; however, one cauliflower field degraded slightly slower than the others. Since a combination of Monitor^R and Metasystox-R was in the same tank mix, the reentry interval was extended to 60 hours. In evaluating the reasons for the slower decay on one cauliflower field, it should be noted that this crop was very young (small) and the maximum rate of 2 pints per acre was applied along with 2 pints per acre of Metasystox-R in 50 gallons of water.

Based on this study, a 24-hour interval would be sufficient to allow safe reentry to a field treated with products containing methamidophos. Other studies conducted by this Branch have indicated the need for a longer reentry interval of 48 hours.

TABLE 1

Monitor^R Degradation Data
(ng/cm^2)

FIELD 1 - Cauliflower

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	N.D.	
Immed. Post	120	100	70	97
24 Hours Post	70	100	60	77
48 Hours Post	31	30	27	29
72 Hours Post	22	16	10	16
6 Days Post	8	17	7	11

FIELD 2 - Cauliflower

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	N.D.	
Immed. Post	43	53	55	50
24 Hours Post	43	38	34	38
48 Hours Post	21	15	18	18
72 Hours Post	----------Not Taken----------			
6 Days Post	----------Not Taken----------			

FIELD 3 - Cauliflower

DAY	REP A	REP B	REP C	Average Residue
Pre-Applicaction	N.D.	N.D.	N.D.	
Immed. Post	504	325	465	431
24 Hours Post	253	259	201	238
48 Hours Post	83	132	64	93
72 Hours Post	73	62	88	74

FIELD 4 - Broccoli

DAY	REP A	REP B	REP C	Average Residue
Pre-Application	N.D.	N.D.	Sample Broken	
Immed. Post	84	105	123	104
24 Hours Post	38	72	73	61
48 Hours Post	67	75	49	64
72 Hours Post	70	17	77	55

MDL = 2 ng/cm^2 (minimum detectable level)
N.D. = none detected

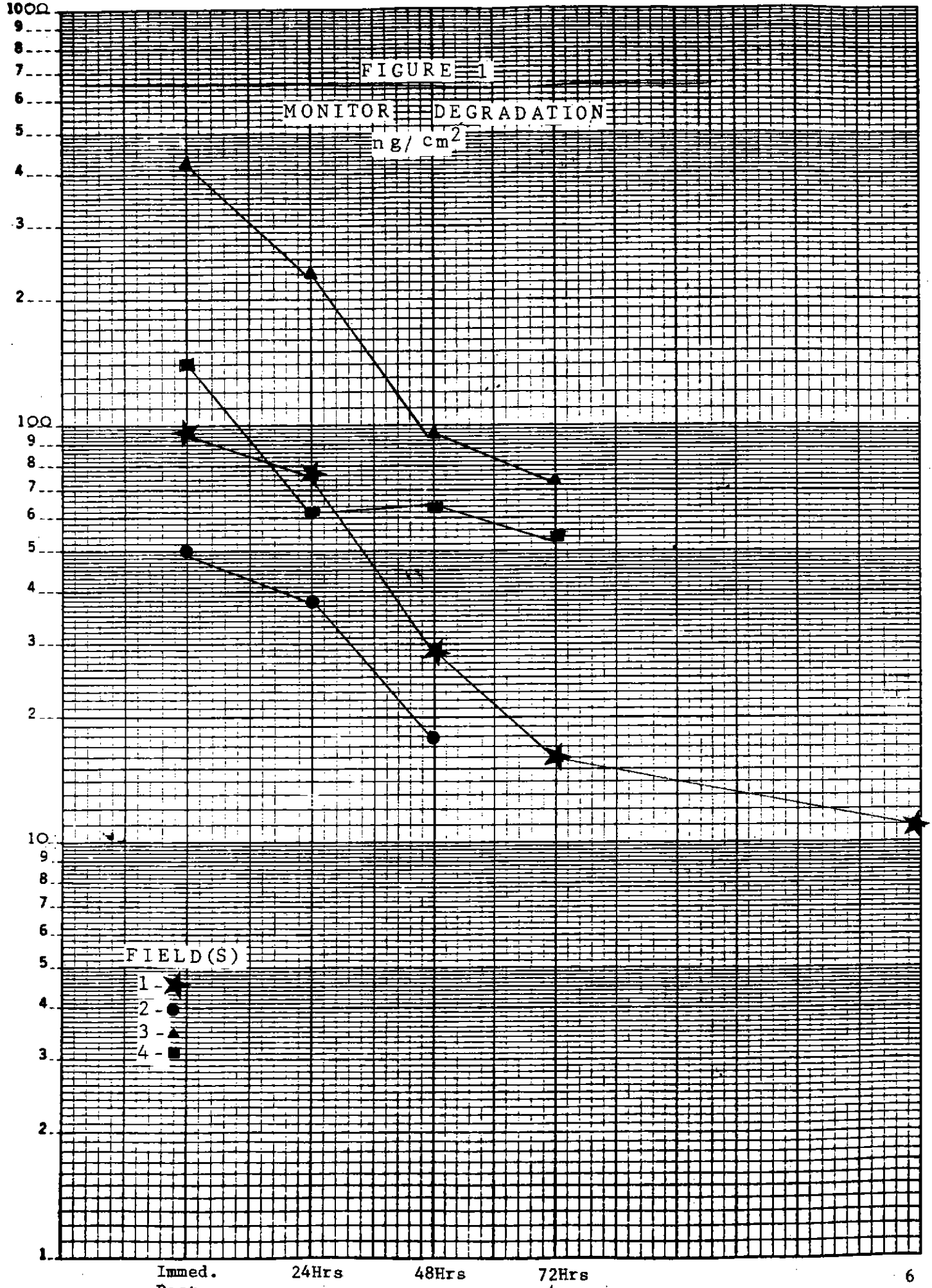
FIGURE 1
MONITOR DEGRADATION
ng/ cm2
100
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
FIELD(S)
1 -
2 -
3 -
4 -
Immed. Post
24Hrs
48Hrs
72Hrs
6 Days

APPENDIX I

ANALYTICAL PROCEDURES FOR THE SCREENING
OF DISLODGEABLE MONITOR^R RESIDUES

SCOPE:

This method is for the dislodgeable analysis of Monitor^R from leaf punch surfaces.

PRINCIPLE:

Monitor^R is washed from leaf surfaces using a water and surfactant solution. The resulting aqueous solution is brought to a known final volume (not to exceed 20 mls) and a 20% aliquot is taken and blended with ethyl acetate and Na_2SO_4. The ethyl acetate is evaporated to a desired volume and analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Distilled water.
2. 2% Sur-ten solution.
3. Ethyl acetate, nanograde. Check for interferences.
4. Na_2SO_4, anhydrous.
5. Analytical standard of Monitor^R:
   a) Stock standard - 1 mg/ml
   b) Working standards - Dilute stock standard to several working standards covering the linear range of the gas chromatograph and the detector used, e.g., 0.01 to 10 ng/ul.
6. Sorval blender, 500 ml capacity blender cup with blade.
7. Boiling flasks, 500 ml capacity.
8. Stemmed, glass funnels.
9. Volumetric test tubes.
10. Graduated cylinders, 250 ml capacity with glass stoppers.
11. Rotoevaporator.
12. Rotator.
13. Gas chromatograph equipped with a nitrogen-phosphorous detector and capillary injection system.
14. A 25 meter of 0.2 mm I.D. SE-54 coated fused silica capillary column.

ANALYSIS:

1. Add 50 mls of distilled water and 0.2 ml of 2% Sur-ten solution to the jar containing the leaf punches.
2. Rotate the jar for 30 minutes.
3. Decant aqueous solution into a graduated cylinder.
4. Repeat steps 1 through 3 twice more.
5. Bring the final volume in the graduated cylinder to 150 mls.
6. Take a 20% aliquot (30 mls) and mix with 150 mls of ethyl acetate in a Sorval blender cup.

7. Add 125 grams of Na_2SO_4 to the cup and blend for 2 minutes on high speed.
8. Decant ethyl acetate through Na_2SO_4 into a 500 ml boiling flask.
9. Add an additional 50 mls of ethyl acetate to the blender cup and blend again on high speed for 2 minutes.
10. Decant ethyl acetate into boiling flask containing the first extract and evaporate to 5 mls.
11. Quantitatively transfer with ethyl acetate into a volumetric test tube and bring to a final volume of 10 mls.
12. Extract is ready for analysis by gas chromatography.

DESORPTION COEFFICIENT:

Recoveries: 10 ug spike - 98%
100 ug spike - 99%

EQUIPMENT CONDITIONS:

1. Gas Chromatograph: HP 5880A
   a) Oven Temperature - 120°C
   b) Injector Temperature - 225°C
   c) Detector Temperature - 250°C
   d) For Capillary Configuration
      i) Column pressure - 15 PSI
      ii) Helium makeup gas flow rate - 25 mls/minute
      iii) Split flow - 40 mls/minute
      iv) Septum purge - 2 mls/minute

CALCULATIONS:

At this time, results are reported in micrograms/cm^2.

REFERENCES

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